Assessment of Secondary Chemical and Mineralogical Trends at Lassen Volcano: Relevance to Early Mars Hydrothermalism

Jordan C. Ludyan, Lindsay J. McHenry

Department of Geosciences, University of Wisconsin-Milwaukee, Milwaukee, WI 53211

UNIVERSITY of WISCONSIN UWMILWAUKEE Department of Geosciences

NASA | WSGC WISCONSIN SPACE GRANT CONSORTIUM

Introduction

- **Placing environmental and astrobiologic constraints on relict hydrothermal** systems identified on Mars relies on our interpretation of geochemical reaction pathways observed in altered terrestrial materials.
- **The Lassen hydrothermal system discharges volatiles from fumaroles that yield** acidic vapor condensates while acidic, oxidizing hot springs precipitate a variety of sulfate minerals and alter substrate into residual silica and phyllosilicates.
- **Analysis of mineralogy and chemical enrichment/depletion trends combined with** in-situ water sampling at hydrothermal sites allows us to place controls on the alteration occurring as secondary mineral phases develop.

Objectives

I. Observe how elemental makeup of substrate (andesite) affects how ions partition into secondary mineral phases in acidic hydrothermal settings.

II. Understand how oxidizing nature of Lassen geothermal waters/vapor condensates impacts mineral diversity.

III. Build upon existing framework for interpretation of proposed hydrothermal sites tentatively identified on the Martian surface through orbital and in-situ measurement.

Water Analyses

- Water analyzed at hot springs and fumaroles in this study reveal environments that are **acidic**, mildly **hot**, and **oxidizing**
- The oxidizing conditions measured via Hydrolab are consistent with presence of significant **sulfate precipitates** and lack of reduced mineral phases

Hydrolab Results; Lassen 2016		T °C	pH	ORP mV	Cond. µS/cm	Salinity psu	TDS g/L
Terminal Geyser	Murky, bubbling hot spring near fumarole	83.4	2.37	+508	9016	4.67	5.4
	Clear hot spring	91.4	3.81	+370	520	0.17	0.2
Pilot's Pinnacle	Murky, bubbling hot spring	84.0	1.71	+576	19615	8.64	9.4
	Bubbling stream-flows through hydrothermal area	33.4	2.21	+715	6884	3.16	3.8

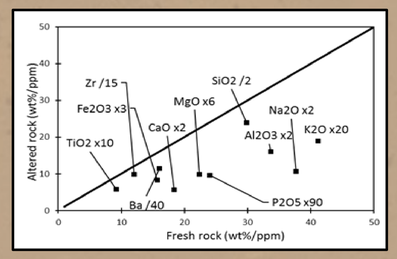
Geologic Context

- **Lassen Volcano:** largest hydrothermal system in the Cascades
  - Discharges **~41kg/s** steam—volcanic vapors and boiled meteoric water **[1]**
- Volcanic materials range from andesite to dacite **[2][3]**

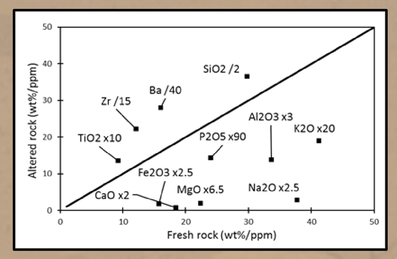
- **Vapor source at depth**—boiled meteoric water undergoes phase-separation **[1][4]**
  - Acidic volatile components(e.g. sulfur) fractionate into vapor phase and emerge as fumaroles at higher elevations
  - Alkaline waters surface at lower elevations as near-neutral, Cl^--rich hot springs

Pilot's Pinnacle: XRF Results

- Relative to substrate, **L-16-PP-07**, a yellow crust, is uniformly **depleted** in all elements analyzed, though likely enriched in sulfur
  - **SiO_2 and TiO_2 insoluble in acidic settings**—sulfur precipitation dilutes this effect
- **L-16-PP-09**, a beige altered clay, shows **enrichment** in **SiO_2**, **TiO_2**, **Ba**, **Zr** but is depleted in all other elements—typical of acid leached samples



Isocon for sample diluted by sulfur **L-16-PP-07**



Isocon highlighting enrichment/depletion trends for **L-16-PP-09** relative to substrate

Mars Hydrothermalism?

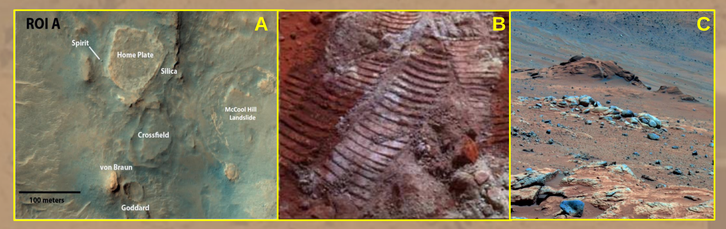
Columbia Hills, Gusev Crater:

A. **SiO2 and TiO2 enrichment** in rocks and soils detected by Mars Exploration Rover (MER) Spirit at Home Plate **[6]**. Chemical/textural features favor biologically mediated **sinter precipitation** vs acid leaching **[7] [8]**

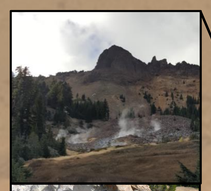
B. Variety of **Fe-, Mg-, & Ca-sulfate minerals** present in Paso Robles class soils near Home Plate suggest **precipitation from fumarolic condensates** with lower water/rock ratios **[9]**

C. ~0.5km from Home Plate—**Carbonate-rich Comanche outcrop** observed—**neutral-pH hydrothermal activity? [10]**

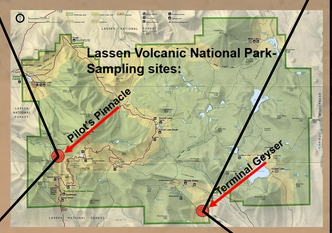
Observations suggest diverse hydrothermal conditions ranging from hot and acidic to more neutral, potentially habitable environments



Field Sites



Oct, 2016—Samples collected in Lassen Volcanic National Park



Both Sites: Acid-Steam Fumaroles & Steam-heated Acid Hot Springs

XRD Results:

		Cristobalite	Amorphous Silica	Tridymite	Quartz	Sulfur	Sodium Alum	Probably alunogen?	Gypsum $CaSO_4 \cdot 2H_2O$	Anhydrite $CaSO_4$	Jarosite $KFe_3(SO_4)_2(OH)_6$	Kalinite $KAl(SO_4)_2 \cdot 11H_2O$	Hexahydrite $MgSO_4 \cdot 6H_2O$	Alunogen $Al_2(SO_4)_3$	Meta alunogen $Al_2(SO_4)_3 \cdot 14H_2O$	Copiapite $Fe^{2+}Fe^{3+}_4(SO_4)_6(OH)_2 \cdot 22H_2O$	Pickeringite/Halotrichite $(Mg,Fe^{2+})Al_2(SO_4)_4 \cdot 22H_2O$	Anatase TiO_2	Montmorillonite $(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$	Nontronite $(CaO_{0.5},Na)_{0.3}Fe_2(Si,Al)_4O_{10}(OH)_2 \cdot nH_2O$	Kaolinite $Al_2Si_2O_5(OH)_4$	Illite (clay-mica)	Albite $NaAlSi_3O_8$	Anorthite $CaAl_2Si_2O_8$	Diopside $MgCaSi_2O_6$
									SULFATES										PHYLLOSILICATES: SMECTITES (2:1)		KAOLINS (1:1)		PRIMARY MINERALS: PLAG		
PILOT'S PINNACLE	L-16-PP-02RIND	x	x		x				x										x				x	x	
	L-16-PP-02SUBSTRATE	x			x					x									x				x	x	x
	L-16-PP-05													x			x		x						
	L-16-PP-06				x	x																			
	L-16-PP-07	x	x		x	x								x		x			x	x	x				
	L-16-PP-08	x												x					x		x				
	L-16-PP-09	x		x		x				x				x					x						
TERMINAL GEYSER	L-16-TG-03				x		x	x					x				x								
	L-16-TG-04		x								x		x	x	x										
	L-16-TG-05				x														x	x	x				
	L-16-TG-06		x		x	x										x		x	x			x			
	L-16-TG-07				x														x					x	x
	L-16-TG-08				x														x	x	x				
	L-16-TG-09		x										x	x			x								
	L-16-TG-10		x									x					x		x						
	L-16-TG-11		x											x					x	x		x			

Analytical Methods

- **Mineralogy:** Mineral and substrate samples were powdered by hand in a mortar and pestle and analyzed using a **Bruker D8 Focus X-Ray Diffractometer** (XRD) **[5]**.
- **Chemical composition:** Dried samples were fused and analyzed using **a Bruker S4 Pioneer X-Ray Fluorescence (XRF) Spectrometer [5]** for major, minor, and trace elements.
- **In-situ water samples:** Water samples were measured for T and pH in the field, and then further analyzed for total dissolved solids (TDS), oxidation-reduction potential (ORP), specific conductivity (Cond), and salinity using a **Hydrolab sonde**.

Implications

- Alteration products at Lassen **dominated by Al-sulfates** and **Al-phyllosilicates**
  - **Lassen andesites are high in Al** (~16.8 wt. %)
  - **Parent lithology significantly impacts alteration products**
- **Martian basalts are high in Fe**
  - **Fe-sulfates and Fe-oxides detected near Home Plate, Gusev Crater [6] [11]**
- Smectites and kaolinite prominent in both sites—**high W/R ratios in acidic settings**
- **S^o prominent near fumarole centers** where samples are in direct contact with acid-steam cloud
- **Mineralogical diversity increases near hot springs** where sulfates precipitate directly from solution

References

[1] Ingebritsen S.E. et al. (2016) *Am. Mineral.* 101, 343-353.
[2] Clynne M.A. (1999), *Journal of Petrology.* 40, 105-32.
[3] Clynne M.A. (2003). USGS Fact Sheet 101-02.
[4] McHenry L.J. et al. (2016) *Am. Mineral.* In Press.
[5] McHenry L.J. (2009) *Chem. Geo.* 265, 3-4.
[6] Squyres S.W. et al. (2008) *Science.* 320, 1063-1067.
[7] Ruff S.W. et al. (2011) *JGR.* 116, E00F23.
[8] Ruff S.W. & Farmer J.D. (2016) *Nat. Commun.* 7, 13554.
[9] Yen A.S. et al. (2008) *JGR.* 113 (6), 1-19
[10] Morris R.V. (2010) *Science.* 329, 421-24
[11] Squyres S.W. (2006) *JGR.* 111 (2)

Thanks to UWM's Office of Undergraduate Research and the Wisconsin Space Grant Consortium for funding and NPS and Lassen Volcanic National Park for access. Also, thanks to my mentor, Lindsay McHenry, and Andy Wanta and Ashley Stewart for help with sample collection